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Acrylic-based composite latexes containing nano-sized liquid crystalline domains

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ABSTRACT

Two-scale multicomposite (meth)acrylate latexes containing nano-sized liquid crystalline domains were synthesized in a two step (mini)emulsion polymerization using a series of methacrylate side chain liquid crystalline monomers and mixture of short chain (meth)acrylates. Detailed characterization of the composite films obtained from the latexes using a combination of DSC, TEM, polarized light microscopy, SAXS and WAXS showed that the liquid crystalline polymers had a layered structure with a 2D-organization that was not perturbed by the amorphous polymer, which on the other hand was partially intercalated between layers. This leads to a two-scale composite with enhanced mechanical properties and higher number of degrees of freedom to fine tune the mechanical properties. The effect of liquid crystalline domains on barrier properties as well as on the water resistance of the films formed from these latexes was also investigated. The persistence of crystalline order of the liquid crystalline polymer phase up to very high temperatures leads to materials with a very broad temperature range of application, improving significantly the performance with respect to other routes based on incorporation of crystalline domains via copolymerization with comb-like monomers.

1. Introduction

Conventional (meth)acrylic polymer latexes have been widely used for coatings, adhesives, paper and textile finishes, cement additives and other applications [1–6]. These polymers exhibit many useful properties but because of their amorphous structure, they are inferior in terms of mechanical properties (toughness), water resistance, barrier properties and durability to polyolefins. It has been shown that these properties can be improved by incorporating crystalline domains in an amorphous (meth)acrylic polymer matrix via crystallization of the lateral alkyl chains of long chain n-alkyl acrylate monomers [7]. The long chain n-alkyl acrylate domains were introduced into the polymer particles via miniemulsion polymerization [8]. However, the temperature range of applications of those polymer latexes is relatively narrow as the melting point of the crystalline domains was only 50 °C. A possible way to expand this range is to incorporate liquid crystalline polymers (LCPs) with high transition temperatures within the polymer particles.

LCPs are a class of materials that combine the properties of polymers with those of liquid crystals (LCs). Generally, LCPs contain a rigid (mesogen) group and semi-flexible (spacer) molecular chains [9–11]. Depending on the placement of the mesogens, the PLCs can be classified into main-chain, side-chain, and combined main- and side-chain LCPs [12]. LCPs have been studied widely in the literature [12–16] and their incorporation into polymer matrices using various processing techniques such as thermal processing (extrusion, injection molding and blow molding) [17–26], solvent casting [20,27] and polymerization [28,29] has been reported. There is plenty of evidence that LCs and LCPs improve the barrier properties of polymers [21–23,28,30,31]. Reinforcement of polymers with LCPs leads to an increase of both the elastic modulus and ultimate strength and to a decrease of the ultimate tensile strain [17,19,26,30,32–35]. Processing conditions and compatibility between LCPs and polymer matrix strongly affect the barrier and mechanical properties of polymer composites [18,19,26,30,32].

Liquid crystalline domains have also been incorporated to

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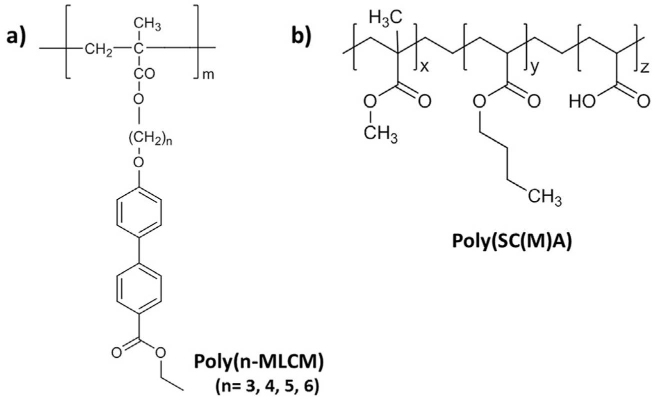
amorphous solvent-borne coatings [36–41]. Thus, Chen et al. [36–38,40] and Athawale et al. [41] synthesized liquid crystalline (meth)acrylic copolymer coatings by grafting *p*-hydroxybenzoic acid to the COOH-functional side chain of the (meth)acrylic copolymers. The same procedure was used by Chiang et al. [39] to synthesize liquid crystalline alkyl resins. In both cases, the coatings containing liquid crystalline domains showed better adhesion to substrates and chemical resistance; higher toughness, hardness and impact resistance; and lower polymer solution viscosity. However, solventborne coatings are under the scrutiny of environmental agencies and are being replaced by waterborne coatings.

In this article, we report, for the first time, on the synthesis, characterization and performance of waterborne polymer coatings containing liquid crystalline domains. The liquid crystalline domains were produced by polymerization of side-chain liquid crystalline monomers. In particular, methacrylate side chain liquid crystalline monomers (n-MLCM) containing biphenyl mesogens with different spacer lengths and a fixed tail, [Ethyl 4'-((n-(methacryloyloxy)alkyl)oxy)-[1,1'-biphenyl]-4-carboxylate]s (n-MLCM; with n = 3, 4, 5, 6, see Scheme 1) were used. The homopolymerization of these monomers leads to a polymeric liquid crystal and the thermal and structural properties of the obtained systems have been reported elsewhere [42]. Since the n-MLCMs are hydrophobic solid monomers with high melting temperature ($T_m > 80$ °C), miniemulsion polymerization has been adapted to synthesize these waterborne semicrystalline latexes. These latexes were used as seed in the semicontinious emulsion polymerization of short chain (meth)acrylates (SC(M)A, a mixture of methyl methacrylate (MMA), n-butyl acrylate (BA) and acrylic acid (AA); MMA/BA/AA = 49/49/2 wt%. With such composition, the resulting composite/hybrid particles contain an amorphous phase with a glass transition temperature (T_g) appropriate for coating applications. We present a thermal and structural characterization of the obtained composite latexes, and study the effect of liquid crystalline domains on their mechanical and barrier properties as well as on the water sensitivity. We finally compare their performance with that of copolymer films containing poly(stearyl acrylate) crystalline domains.

2. Experimental section

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA, Quimidroga), n-butyl acrylate (BA, Quimidroga) and acrylic acid (AA, Aldrich) as short chain (meth)acrylates (SC(M)A) monomers were used as received. A series of methacrylate side chain liquid crystalline monomers (n-MLCM (n = 3–6)) were synthesized as described elsewhere [42] and used in this study. Potassium persulfate (KPS, Aldrich) as water soluble radical initiator and alkyldiphenyloxide disulfonate (Dowfax™ 2A1, The Dow Chemical Company) as anionic surfactant were used as received. Deionized water was used as polymerization medium.



Scheme 1. Chemical formulae of a) n-MLCM homopolymers and b) short chain (meth) acrylates (SC(M)A) copolymer.

2.2. Synthesis of the composite latexes

A seeded semicontinious emulsion copolymerization was used to synthesize the composite latexes containing the liquid crystalline polymers. In the first step, a latex of liquid crystal polymer was formed by miniemulsion homopolymerization [43] of n-MLCM. It is worth pointing out that short chain (meth)acrylates monomers cannot be added at this stage because this would preclude the formation of liquid crystalline domains. A solution of n-MLCMs in chloroform was added to an aqueous solution Dowfax 2A1 (3 wt% based on all monomers) and mixed for 10 min. The coarse emulsion was sonicated by using a Hielscher Sonifier (UIS250v, amplitude 100 and energy pulsed at 1 Hz) over 10 min in an ice bath to avoid overheating. The n-MLCM miniemulsion was purged with nitrogen and the miniemulsion homopolymerization was carried out in batch by using KPS (1 wt% based on n-MLCM) at 70 °C for 3 h in a 50 ml flask immersed in an oil bath and equipped with a magnetic stirrer. Afterwards, the chloroform was removed completely by rotary evaporation. The second step was carried out in a Miniplant M100 setup (Chemspeed Technologies) in 100 ml stainless steel reactors equipped with nitrogen inlet and a stainless steel anchor-type stirrer (200 rpm were used in the polymerizations). The poly(n-MLCM) latex produced in the first step was transferred to the reactor, purged with nitrogen and heated to the reaction temperature (70 °C). Then, the aqueous solution of initiator (KPS, 1 wt% based on the second stage monomers) was added as a shot and the mixture of SC(M)A monomers was fed to the reactor under starved conditions during 3 h. The reactions continued for 1 h in batch.

To study the effect of the polymer liquid crystal domains on the properties of the latexes, two series of experiments were designed (Table 1). In Series A, 6-MLCM (crystalline monomer with 6 CH_2 units in the spacer) was used and the ratio of poly(6-MLCM)/poly(SC(M)A) was varied (20/80 and 30/70 wt/wt). This series also includes the homopolymer of 6-MLCM as a reference. In Series B, the ratio poly(n-MLCM)/poly(SC(M)A) was 20/80 wt/wt and the length of the spacer was varied (3, 4, 5 and 6 CH_2 units).

In addition, a latex devoid of liquid crystalline domains was synthesized by semibatch emulsion copolymerization and used as reference to study the effect of incorporating liquid crystalline domains in the particles. In this case, the reactor was charged with the aqueous phase containing Dowfax™ 2A1 (3 wt% based on monomer), purged with nitrogen and heated to the reaction temperature (70 °C). Then, the initiator (KPS, 1 wt% based on all monomers) solution was added as a shot and the mixture of SC(M)A monomers was fed to the reactor during 3 h. Copolymerization continued for 1 h in batch (Run C in Table 1).

2.3. Characterization

Monomer droplet and polymer particle sizes were measured by dynamic light scattering (DLS) using a Zetasizer Nano Series (Malvern Instruments Ltd.). The values given are z-average values obtained through cumulants analysis. The equipment was operated at 20 °C and the values reported are the average of two repeated measurements.

Only a fraction of the poly(n-MLCM) was soluble in tetrahydrofuran (THF) at room temperature. The molecular weight distribution (MWD) of the soluble fraction was determined by gel